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TUNABLE SURFACE WETTABILITY OF CARBON NANOTUBES-NONWOVEN TEXTILE COMPOSITES

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Abstract
Tunable surface wettability of a material may have a valuable role in environmental application. We created a composite material from a nonwoven textile (NW) decorated with carboxylic functionalized carbon nanotubes (*f*-CNT) using a vacuum filtration method. The surface wettability of the composites is tunable by the *f*-CNT amount. Surface wettability was checked by contact angle measurements. The morphology of the samples was observed by scanning electron microscopy. The isoelectric point of *f*-CNT was determined from electrophoretic mobilities measurements. This composite material with tunable wetting properties may be relevant *e.g.* in water purification.

Introduction
Carbon nanotubes are widely known in the sciences since Ijima's work [1]. CNTs have a wide range of application in the wastewater treatment. CNT based materials like the CNT sponges are applicable *e.g.* for oil absorption due to the large surface area and excellent flexibility, furthermore they are light-weight [2]. The functionalization is a good opportunity to tune or modify some property of CNTs [3]. The overlapped nanotubes in a group of CNT make bulges on the surface. The liquid follows or suspends on the highest part of the bulges which eventuates 'Wenzel' or 'Cassie-Baxter' states, respectively [4,5]. The chemical properties (hydrophilic or hydrophobic) of the substance and the extent of surface roughness can control these wetting regimes [6].

Experimental
Materials:
Multiwalled carbon nanotubes (MWCNT) were synthesized and then it was modified with an oxidative functionalization to create carboxylic groups on the outer shell of the tubes. The MWCNTs were synthesized by 2 h of catalytic chemical vapor deposition from a C_2H_4:N_2 (30:300 cm^3/min) gas mixture at 650 °C by using Fe,Co/Al_2O_3 catalyst (metal loading: 2.5-2.5 m/m%). The synthesized materials were purified by repeating 4 h of refluxing in 10 mol/dm^3 aqueous NaOH, then 4 h in cc. HCl solution four times. A part of the as prepared pristine non-functionalized carbon nanotubes (*nf*-CNT) were subjected to oxidative chemical functionalization (8 h reflux of 4 g CNT in 500 cm^3 cc. HNO_3 solution). After that, further functionalization was carried out to facilitate surface carboxyl group formation and improve their hydrophilicity to get so called functionalized carbon nanotubes (*f*-CNT). During this step, the suspension of the previously received nanotubes (10 g/dm^3 CNT) were sonicated in a 0.1 mol/dm^3 solution of $KMnO_4$ in 60% aqueous perchloric acid for 15 minutes. The excess $KMnO_4$ was then reacted with oxalic acid. The fabricated CNTs were washed first in 0.01 mol/dm^3 hydrochloric acid to remove MnO_2, afterward in deionized water, then finally dried in air at 80 °C for 24 h.
A circular piece (d=25 mm) of a needlepunched polyester nonwoven material (fibre length of 48 mm; fibre diameter of 29 μm) was used to prepare fCNT-NW composites. An as-prepared *f*-CNT (in deionized water) suspension was filtrated through the nonwoven material by a dead-

end filtration equipment (see in Fig 1.). Three samples were fabricated with nominal *f*-CNT loadings of 5, 10, and 15 wt%. The corresponding sample IDs were assigned as 'fCNT-5-NW', 'fCNT-10-NW' and 'fCNT-15- NW', respectively. Furthermore, an 'fCNT-film' was also prepared in the same manner, just without NW.

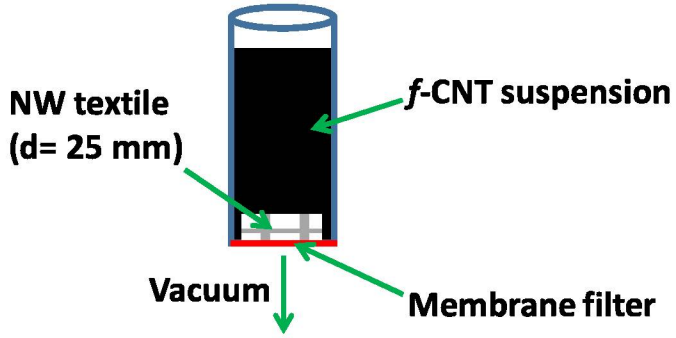

Figure 1. Schematic of the preparation process of the composites.

Methods:

The *f*-CNTs were characterised by **transmission electron microscopy** (TEM). It was performed on a FEI Tecnai G^2 20 X Twin instrument operated at a 200 kV accelerating voltage. The suspension of the sample was dropped onto copper mounted holey carbon standard TEM grids. Several different positions were examined on each sample and images were taken at each position.

Electrophoretic mobilities of the *f*-CNTs were measured in a Nano ZS (Malvern) apparatus with a 4 mW He–Ne laser source (λ = 633 nm) using disposable zeta cells (DTS 1070) at 25±0.1 °C. The zeta-standard of Malvern (−55±5 mV) was used for calibration and the samples were diluted to give an optimal intensity. To get comparable data, the dispersions were homogenized in an ultrasonic bath for 10 s, after which 2 min relaxation was allowed. The effect of pH variation was studied at 10 mM NaCl. The Smoluchowski equation was applied to convert electrophoretic mobilities to electrokinetic potential values. The accuracy of the measurements was ±5 mV.

Morphology of fCNT-NW composites was determined by **scanning electron microscopy** (SEM). For these measurement a Hitachi S-4700 microscope was used equipped with a field emission gun operated with accelerating voltages of 10 kV.

Apparent equilibrium contact angles were measured by placing a 10 µL water droplet (coloured with methylene blue dye) onto the surface investigated. Six independent images (recorded at room temperature by Dino-Lite Edge Digital Microscope; AnMo Electronics Corp.; product code AM4815ZTL) were analyzed for all samples using the ImageJ® system.

Results and discussion

The typical length of the *f*-CNTs was over 10 µm and their outer diameter fell in the 15-25 nm range as determined from TEM image analysis (see in Fig. 2.).

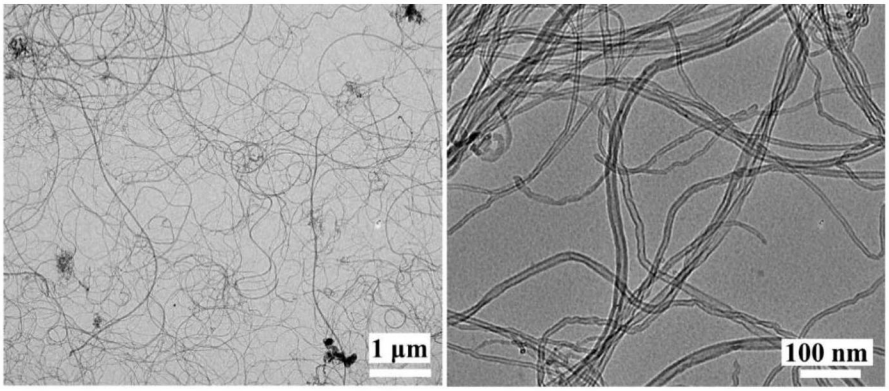

Figure 2. TEM images about *f*-CNT.

Three different composites were prepared, which contain different amount of *f*-CNT. During filtration, a big fraction of *f*-CNT were deposited on the top surface of the nonwoven textile which can be seen in Fig. 3. There is more carbon nanotube on the NW with increasing amount of CNT. While there is some ensemble of *f*-CNT in case of fCNT-5-NW (Fig. 3.b.), however CNTs completely cover the textile surface in case of fCNT-15-NW (Fig. 3.d.). Dual scale surface roughness is experienced on the top of the composites, because the textile fibres are in micron-scale while the CNT is in nano-scale. The top surface of the composites is rough and fractured.

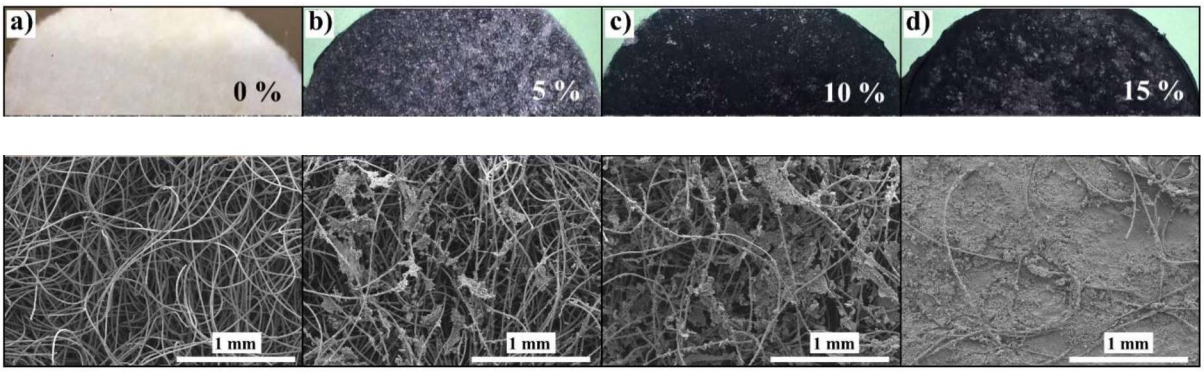

Figure 3. Digital photos (above) and SEM images (below) about fCNT-NW samples.

The zeta potential of the *f*-CNTs is plotted as a function of pH in Fig. 4. The isoelectric point (IEP, at which the net charge of CNT is zero) is at pH~2. The values of zeta potential shift to more negative region with the increasing pH caused by the deprotonation of the –COOH functional group of *f*-CNT.

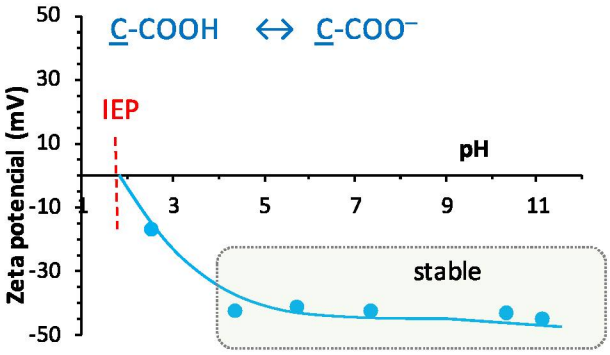

Figure 4. The pH dependent zeta potential of *f*-CNT samples (10 mM NaCl, 25°C).

Apparent contact angles were measured to determine the hydrophilic-hydrophobic nature of the materials. Some representative photos about the water droplets coloured by methylene blue on the surface of pure textile, composite sample and fCNT-film can be seen in Fig. 5.

Figure 5. Some representative photos about the coloured water droplets.

The fCNT-film has the most hydrophilic properties as the average contact angle is found to be 43.3°. The pure NW sample shows hydrophobic nature with contact angle of 132.8°. If the *f*-CNT loading was increased, the contact angle was decreasing in case of composites as it is depicted in Fig. 6. Presumably, there was not a uniform covering with *f*-CNT in case of fCNT-5-NW sample, which leads to the dominance of Cassie-Baxter regime, due to the lower surface energy of the polyester fibres and three dimensional texture of the NW material.

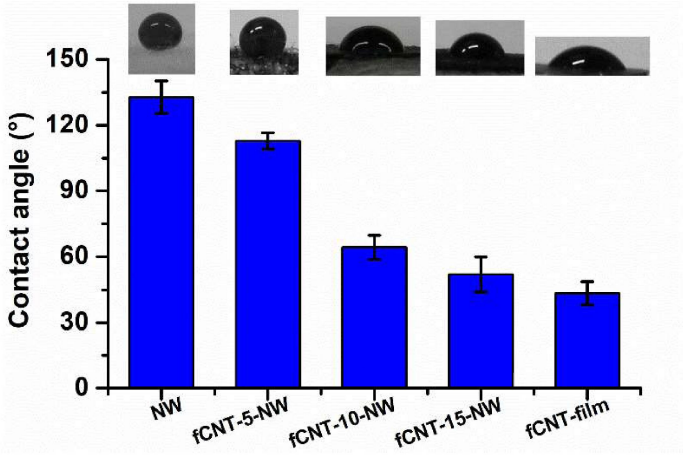

Figure 6. Average contact angles (from 6 droplets, V=10 µL) with digital photos of droplets on the surface of the materials.

Conclusion

In this work it was prepared some composite sample that are carboxylic functionalized MWCNT decorated needlepunched polyester nonwoven textiles by a scalable and inexpensive vacuum filtration process. The carboxylic functionalization of MWCNT results in a more hydrophilic nature of CNT. Apparent contact angles prove, that the functionalized carbon nanotube loading to the nonwoven textiles can tune the hydrophobic-hydrophilic characteristics of the composites. The surface wettability can be controlled by a predefined amount of *f*-CNT. Therefore, it may have a potential role *e.g.* in the wastewater treatment.

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